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Review

Photosystems and global effects of oxygenic photosynthesis ☆

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ABSTRACT

Because life on earth is governed by the second law of thermodynamics, it is subject to increasing entropy. Oxygenic photosynthesis, the earth's major producer of both oxygen and organic matter, is a principal player in the development and maintenance of life, and thus results in increased order. The primary steps of oxygenic photosynthesis are driven by four multi-subunit membrane protein complexes: photosystem I, photosystem II, cytochrome b_6f complex, and F-ATPase. Photosystem II generates the most positive redox potential found in nature and thus capable of extracting electrons from water. Photosystem I generates the most negative redox potential found in nature; thus, it largely determines the global amount of enthalpy in living systems. The recent structural determination of PSII and PSI complexes from cyanobacteria and plants sheds light on the evolutionary forces that shaped oxygenic photosynthesis. This newly available structural information complements knowledge gained from genomic and proteomic data, allowing for a more precise description of the scenario in which the evolution of life systems took place. This article is part of a Special Issue entitled: Regulation of Electron Transport in Chloroplasts.

1. Introduction

Oxygenic photosynthesis—the use of light energy to synthesize ATP and NADPH resulting in the production of oxygen from water—underpins the survival of virtually all higher life forms on earth. Producing oxygen and assimilating carbon dioxide into organic matter determines, to a large extent, the composition of our atmosphere and provide all life forms with essential food and fuel. The oxygenic photosynthesis that operates in cyanobacteria, algae, and plants is catalyzed by four biochemically defined membrane complexes [1,2]. According to the partial reactions that they catalyze, PSII is defined as a water–plastoquinone oxidoreductase, cytochrome b_6f complex as a plastoquinone–plastocyanin oxidoreductase, PSI as a plastocyanin–ferredoxin oxidoreductase, and F-ATPase as a proton-motive force (pmf)-driven ATP synthase [1,2]. PSI and PSII contain chlorophylls and other pigments that harvest the light and funnel its energy to photosynthetic reaction centers (RCs). Energy captured by the RC induces the excitation of a special chlorophyll pair, which initiates the translocation of an electron across the membrane through a chain of cofactors [1,2]. Water, the electron donor for this process, is oxidized to O_2 and four H^+ by PSII. The electrons extracted from water are shuttled through a quinone pool and the cytochrome b_6f complex to plastocyanin, a small soluble copper protein. Solar energy absorbed by PSI induces the translocation of an electron from plastocyanin at the inner face of the membrane (lumen) to ferredoxin on the opposite side (stroma). The charge separation in PSI and PSII, together with the electron transfer through the cytochrome b_6f complex, leads to the formation of an electrochemical potential, which powers ATP synthesis by the fourth protein complex, F-ATPase. In the "dark", the generated ATP and NADPH catalyze CO_2 reduction to carbohydrates [2].

About 4 billion years ago, at the onset of life on earth, our planet (like the universe) was in a highly reducing state. Under these "anaerobic" conditions, the elements were suspended in their inert, reduced-valence states. Thus, the atmosphere was rich in nitrogen in the form of ammonia (NH_3) or N_2, carbon as CO or CO_2, and oxygen as H_2O [3]. The surface was covered by water and the minerals, including metal ions, were in a state of reduced valence. All of this changed drastically with the onset of oxygenic photosynthesis; this event has been called the "big bang of evolution" [4].

2. Photosynthetic reaction centers

Photosynthetic reaction centers (RCs) comprise a chlorophyll pair capable of oxidation–reduction reactions, antenna chlorophylls, and other pigments that harvest light quanta and deliver the excitation to the chlorophyll pair. For an unknown mechanistic reason, the chlorophyll dimer capable of oxidation–reduction activity evolved from a homodimeric protein, with each monomer donating one chlorophyll molecule [5–8]. Photosynthetic reaction centers are generally divided, according to the identity of their terminal electron acceptor, into two groups: RC type I (RC1) with an Fe–S cluster as the terminal acceptor (e.g., photosystem I [PSI] of oxygenic photosynthesis and the RC of green sulfur bacteria and heliobacteria) and type II

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(RC2), with a mobile quinone as the terminal acceptor (e.g., photosystem II [PSII] of oxygenic photosynthesis and the RC of purple and green filamentous bacteria) [9]. Phylogenetic analyses of the core reaction center proteins of PSI and PSII from cyanobacteria and higher plants reveal several striking structural similarities that are also held in common with the type I RC of green sulfur bacteria and the type II RC of purple bacteria [10–12]. These similarities support the long-standing hypothesis of a common evolutionary origin for all reaction center complexes [5,11,13–15]. A basic structural difference between extant RC1 and extant RC2 is that in RC1 (including PSI), the core protein contains both electron transfer components and intrinsic antenna chlorophylls within its 11 transmembrane (TM) helices. In PSII, these functions are split among different proteins; accordingly (RC2 of purple and green filamentous bacteria has a smaller number of TM helices). The PSII intrinsic antenna proteins CP43 and CP47 have primary sequence resemblances to the antenna domain in the core protein of chlorobium and heliobacteria RC1, but not to any purple bacteria protein. In accordance with these differences and similarities, an evolutionary scenario emerges in which the ancestral photosynthetic reaction center began with a gene encoding a large protein that operated as a homodimer [5–10], much like PscA of the *Chlorobiaceae* (Fig. 1). Each monomer was capable of binding 20–40 bacteria-type chlorophyll molecules, of which two were held in close proximity in an environment conducive to forming an excitation trap capable of oxidation–reduction reactions [9]. On the opposite side of the membrane, there were two identical quinone-binding sites (one for each monomer). A strategically located cysteine residue in each monomer provided a template for the formation of the electron-acceptor nonheme iron center. This version of the reaction center would have been capable of functioning much like RC2 of extant purple bacteria with regard to cyclic electron transport for ATP production, and like type I RCs such as current PSI (Fig. 1). This reaction center would have been operating under the anaerobic conditions that governed the atmosphere during the onset of life on earth. At that time, reducing substances were abundant, and due to the lack of free oxygen, ATP could not be formed by respiration. Cyclic photophosphorylation was the main source of ATP for photosynthetic organisms.

Possible scenarios for the evolution of the primordial homodimeric RC into the current PSI and PSII-like reaction centers were discussed elsewhere [8–12]. However the evolutionary driving force that led PSII to extract tightly held electrons from water under anaerobic condition where plentiful electrons are readily available is totally obscure. Was it opportunistic event due to the emergence of chlorophyll a or the growth of enceinte bacteria in a highly oxidized ecological niche and subsequent taking advantage of the oxygenic environment that they generated, is not clear?

3. Structure of PSII and oxygen evolution

Substitution of bacterial chlorophyll with chlorophyll a in RC2-like reaction center generated novel operating energy levels for photosynthesis. A far greater amount of energy was converted for each excited electron, which provided an opportunity for novel photochemical reactions to take place. A potential as oxidizing as +1 V could be generated, allowing evolution of machinery that could oxidize water at +0.9 V. The main obstacle for the evolution of such a process was the need to extract four electrons from two water molecules to yield an oxygen molecule. Studies in the last two decades have established the components involved in oxygen evolution (along with some of their redox potentials) at equilibrium, but not under the conditions in which they normally operate [2,13–15]. The pathway of electron transfer in PSII is generally agreed to be as follows: $H_2O \rightarrow [Mn_4CaCl] \rightarrow Y_Z/Y_Z\bullet \rightarrow P680/P680^+ \rightarrow Pheo_a/Pheo_a^- \rightarrow Q_A/Q_A^- \rightarrow Q_B/Q_B^-$. Where $[Mn_4CaCl]$ is the manganese cluster, Y_Z is a tyrosine residue that mediates electron transfer between the manganese cluster and the chlorophyll pair P680, $Pheo_a$ is a pheophytin, and Q_A and Q_B are plastoquinones. The estimated redox potentials of the intermediates in PSII are: $P680^+/P680$ +1.12 V, $Y_Z\bullet/Y_Z$ +0.97 V, O_2/H_2O +0.93, $Pheo_a^-/Pheo_a$ −0.64 V, Q_A^-/Q_A −0.03 V and Q_B^-/Q_B 0.03 V. The manganese cluster accumulates four positive charges in four consecutive rounds of photon captures to accomplish water oxidation. According to the catalytic cycle proposed by Joliot and Kok, photosynthetic oxygen evolution involved multiple elementary steps [16–18]. Starting from the dark stable S1 state, the OEC is

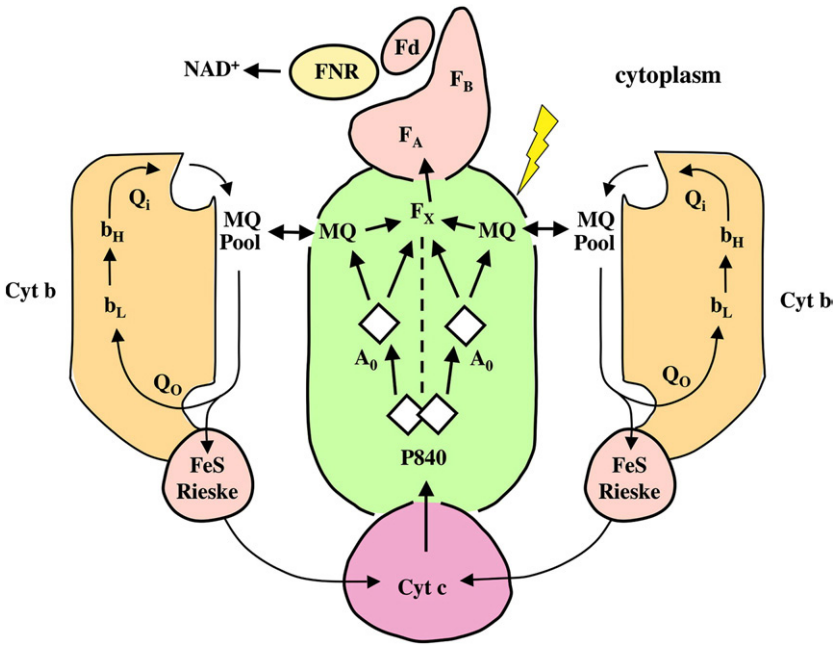

Fig. 1. A schematic depiction of homodimeric reaction center. Sunlight energy is converted into a negative redox potential that is used for reduction of substances such as CO_2 and cyclic electron flow that generate membrane potential and proton gradient that is utilized for ATP formation. Arrows indicate the direction of electron flow. P840 is the primary electron donor. Ao is the primary electron acceptor. MQ, menaquinone. Fx, Fe–S center "X". FA and FB, are Fe–S centers "A" and "B". Fd, ferredoxin. FNR, ferredoxin–NADP-reductase. Cyt b, cytochrome *b*.

advanced by single-electron steps to a sufficiently high oxidation state that reacts with H_2O to form O_2. Each state along this cycle is called a 'storage-state (S)', with S0 representing the most reduced state of the oxygen-evolving complex and S4 the most oxidized state. In the dark, all S-states spontaneously convert to the S1 resting state within minutes. Recent relatively high-resolution structures of PSII from cyanobacteria have revealed the position of most (if not all) of the substances involved in oxygen evolution, but the precise function of each one in the formation of the S-states is debated [19–21].

The recent PSII crystal structures from the cyanobacterium *Thermosynechococcus elongatus* were solved at 2.9 and 3.5 Å resolution [22,23]. They have provided a wealth of information about subunit structures, pigment arrangement, lipid organization, and cofactor positions. The crystal structures of PSII enabled the assignment of up to 20 protein subunits, 35 chlorophyll a molecules, 12 carotenoid molecules, 25 integral lipids, and the two electron-acceptor plastoquinone molecules. The location of the Mn_4Ca cluster fit well with the electron density, as did one chloride that was modeled at a distance of 6.5 Å from the manganese cluster. Fig. 2 depicts a top view of the PSII monomer and the electron transfer chain (ETC) components. In all crystal structures, PSII appears as a dimer, and it was assumed that this form predominates *in vivo* [21,22]. However this notion was recently challenged and it was suggested that the cyanobacterial PSII might operate as a monomer [24]. The structure of the PSII monomer (Fig. 2a) reveals several organizational features of the pigments and prosthetic groups. The ETC is situated in the center, and is quite isolated from the two antenna chlorophyll bundles organized in 2-fold symmetry along the sides of the complex. Relatively large numbers of carotenoids and lipids are situated among and in proximity to the chlorophyll bundles, but they are not present at close proximity to the ETC. The area surrounding the ETC is populated almost exclusively by the amino acids of the central subunits.

Crystal structures have provided a clear and detailed view of all of the light-induced electron transport and oxygen evolution components, paving the way to solving the mechanism of one of the most important reactions in nature. However, till very recently the precise positions of the manganese ions and water molecules were uncertain in current X-ray diffraction models, because the coordinate error in the density maps is often as high as 1 Å. Therefore, X-ray models of the manganese metal center have relied upon both overall electronic density maps and manganese–manganese distances, as determined by X-ray absorption spectroscopy [21,25,26]. Fig. 2b depicts a side view of the PSII ETC that essentially performs light-induced oxygen evolution. The main challenges that must be met before this reaction can be fully understood are to decipher each of the four single-electron oxidation states in terms of S-states, the valence of each of the manganese atoms, and the participation of the water molecules and protons. An enormous amount of scientific work has been devoted to this subject, yet there is no general consensus among the results yielded by the various sophisticated methods that have been used to investigate it [18–26].

The challenge of collecting solid structural data that will clearly differentiate correct from incorrect hypotheses regarding the mechanism of oxygen evolution is enormous. A structure of better than 2 Å resolution at two intermediate states (S1 and S3) that are undamaged by the X-ray irradiation is desirable. Because of the irresistible intellectual challenge and the critical importance of the mechanism of oxygen evolution, it may be achieved before too long. Indeed very recently an atomic-resolution model at 1.9 Å of PSII from *Thermosynechococcus vulcanus* was presented in The 15th International Congress of Photosynthesis (Shen, J-R., Umena, Y., Kawakami, K. and Kamiya, N. pp. 87 in the Abstracts). The atomic resolution revealed the exact position of the 4 Mn and Ca cluster in the water-oxidizing center that was close to that proposed by Ferreira et al. [22]. The distances between the Mn and Ca atoms and their precise interactions with the surrounding amino acids and water molecules revealed.

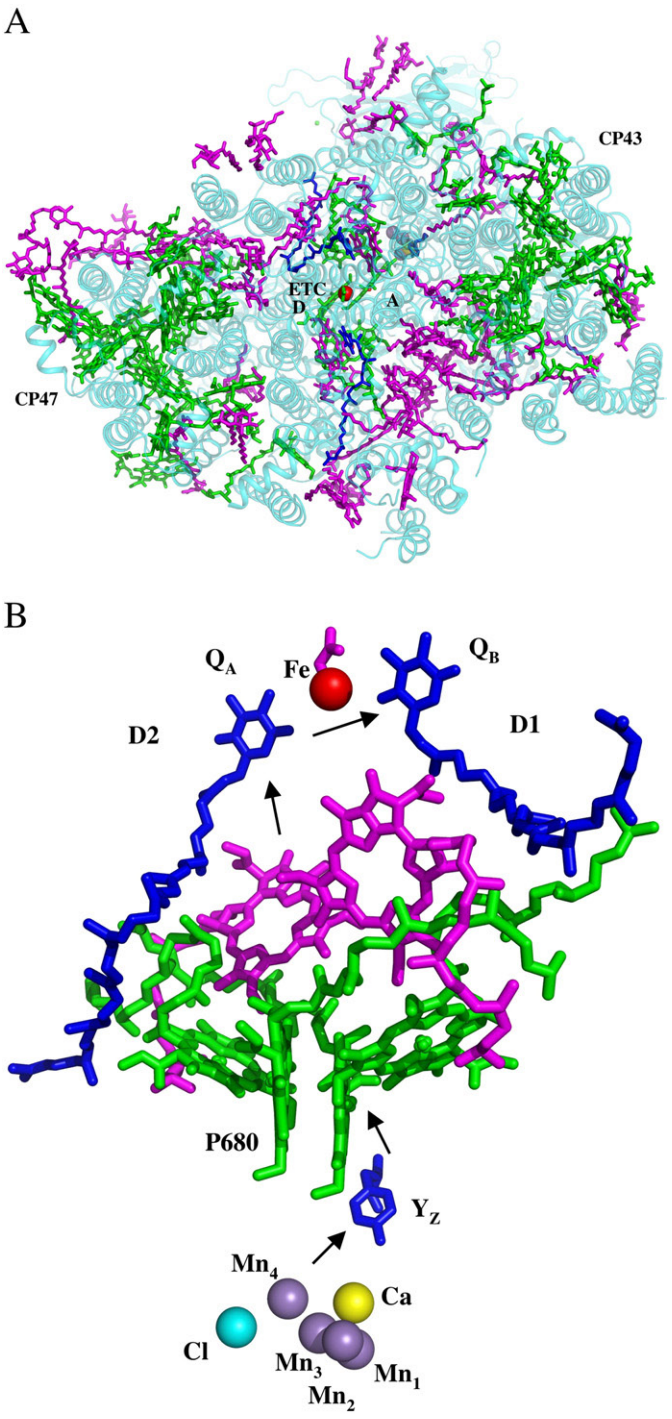

Fig. 2. A structural model of the cyanobacterial PSII. a. View from the cytoplasm of the PSII monomer. The model was constructed according to Guskov et al. [23], PDB 3BZ1. Green, chlorophylls; cyan, all the other pigments and prosthetic groups. ETC is colored as in (b). b. Side view of the electron transfer components and the oxygen-evolving complex. Green, chlorophylls; magenta, pheophytin; blue, plastoquinone; red, iron; blue, Y_Z—tyrosine 161/D1; cyan, chloride; yellow, calcium; purple, manganese.

4. The structure of plant PSI

Two major breakthroughs in unraveling PSI were the 2.5 Å resolution X-ray crystal structure of trimeric PSI from the

cyanobacterium *T. elongatus* [27] and the 4.4 Å resolution intact PSI–LHCI super complex from the pea (*Pisum sativum*) [28]. This was the first time that the subunit composition, as well as the architecture of the cofactors and the antenna system, was identified. While the cyanobacterial PSI is composed of 12 subunits harboring 96 chlorophylls, the plant PSI contains at least 17 subunits and over 170 chlorophyll molecules [27,28]. Plant PSI is essentially composed of two membrane complexes: (1) the core complex, also referred to as the RC complex, where the bulk of light capturing and charge separation reactions take place and (2) the light-harvesting complex I (LHCI), which serves as an additional antenna system that maximizes light harvesting by collecting solar radiation and transmitting the excitation to the core complex [27–34]. The two complexes can be dissociated readily by Triton X100 or Zwittergent-16 treatment and separated on a sucrose gradient [35,36]. Therefore, it is extremely challenging to obtain intact PSI that contains the two complexes in a crystallizable state and still has higher order in all its components. Despite the fact that plant PSI has been crystallized and solved at 3.4 Å resolution, this challenge has not yet been satisfactorily met, and the quality of the structure of the LHCI portion of the super complex leaves much to be desired [29]. Many factors had to be optimized to achieve 3.4 Å resolution. A significant improvement in the diffraction quality was achieved by using a controlled dehydration process. Dehydration was performed by soaking the crystals in gradually increasing concentrations of the precipitating agent from about 5% to 40% PEG 6000 throughout several intermediate steps, each one with an incubation time of up to 24 h. This post-crystallization soaking shrank crystals to the apparent minimum of variable unit-cell dimensions, decreasing the cell volume by about 30%. All of the crystals exhibited a space group of P21 that not only had variable cell dimensions, but also had different β that varied from 91° to 98°. We observed that concomitant with increasing the quality of the RC structure, the quality of the LHCI structure decreased. The model of plant PSI depicted in Fig. 3 is constructed of two separate datasets, one

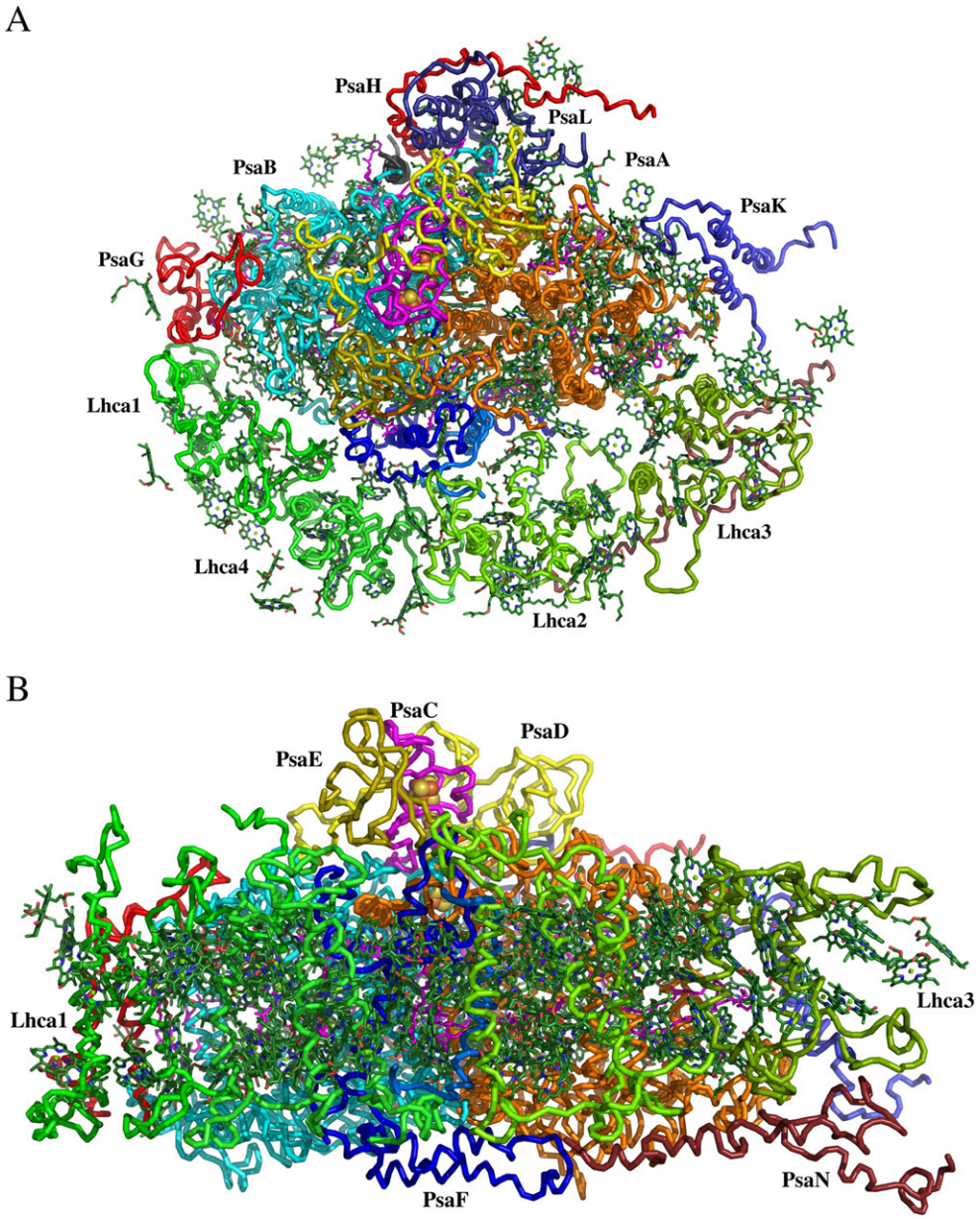

Fig. 3. A structural model of plant PSI. a. View from the stroma of the structure of plant PSI. Each individual subunit is colored differently. Chlorophylls are in green. Carotenoids in magenta and quinones in blue. Some of the individual subunits are indicated. b. A side view of plant PSI.

from crystals of β 98° at 3.1 Å resolution for the RC, and the other from crystal of β 91° at 3.3 Å resolution, which yielded a better LHCI structure [37]. The RC of plant PSI contains 12 polypeptides (PsaA, PsaB, PsaC, PsaD, PsaE, PsaF, PsaG, PsaH, PsaI, PsaJ, PsaK, and PsaL) and approximately 100 chlorophyll molecules. The plant RC retains the location and orientation of the electron transfer components and all of the cyanobacterial transmembrane helices except for subunits X and M, which are not present in plants. Attesting to the antiquity of the chlorophyll arrangement in the RC, the crystal model of plant PSI reveals that the majority of the RC chlorophylls retained the same position and tilting angle as in PSI from the cyanobacteria *S. elongatus* [27,28]. Together with PsaG, PsaH, PsaN, and Lhca1–4, the recent structure reveals 18 protein subunits, with PsaO and PsaP, which were recognized by biochemical means as subunits of PSI, missing from the structure. The new structure also revealed 173 chlorophyll molecules, 109 with orientation of the Qx and Qy transition dipolar moments and 51 with full-length phytol [37]. Eighteen carotenoids were also built into the model. There are a few pertinent questions that the current PSI model cannot address: Does PSI's complexity belie its efficiency? Where exactly are the red traps situated, and how do they contribute to the efficiency of the system?

5. Structural evolution of PSI

The evolutionary scenario of PSI, depicted in Fig. 4, begins with a hypothetical homodimeric reaction much like the one that operates in *chlorobiacae* [5,6], except that it contains chlorophyll a, like the current PsaA. PsaC, with its two iron sulfur clusters, serves as a terminal electron acceptor. Gene duplication and separate evolution generated a heterodimer composed of PsaA, PsaB, and PsaC. The current PSI of cyanobacteria and higher plants evolved by sequential addition of novel subunits that fulfilled functions necessitated by advances in the evolution of the core PSI in the various organisms. In the next step, PsaD and PsaE were added to shape the electron-acceptor side of PSI as we know it today. Then, with the addition of PsaF, the electron donor side gained its specificity for soluble cytochromes and plastocyanin. All of these evolutionary steps are yet to be found in any extant organism. Recently, an operon encoding PsaA, PsaB, PsaC, PsaD, PsaE, PsaK, and a PsaJ–PsaF fusion protein was discovered in marine viruses [38]. This suggests that such a PSI reaction center existed in primitive cyanobacteria, too (Fig. 4). The next evolutionary step was the addition of PsaL and PsaI, which are present in PSI of cyanobacteria and plants; we suggest that this step was the point at which the two photosystems branched apart. Possibly driven by living at low light intensities, cyanobacterial PSI evolved further by adding PsaM and PsaX and forming a trimeric reaction center [8]. Green algae and plants are mainly present near the surface of oceans and on land. To adapt to high light intensities, their PSI was rendered monomeric; the addition of PsaH was critical for this event [28]. The addition of PsaG to the pole opposite PsaK served as an evolutionary template for the assembly of the four light-harvesting chlorophyll–protein complexes Lhca1, Lhca4, Lhca2, and Lhca3. The

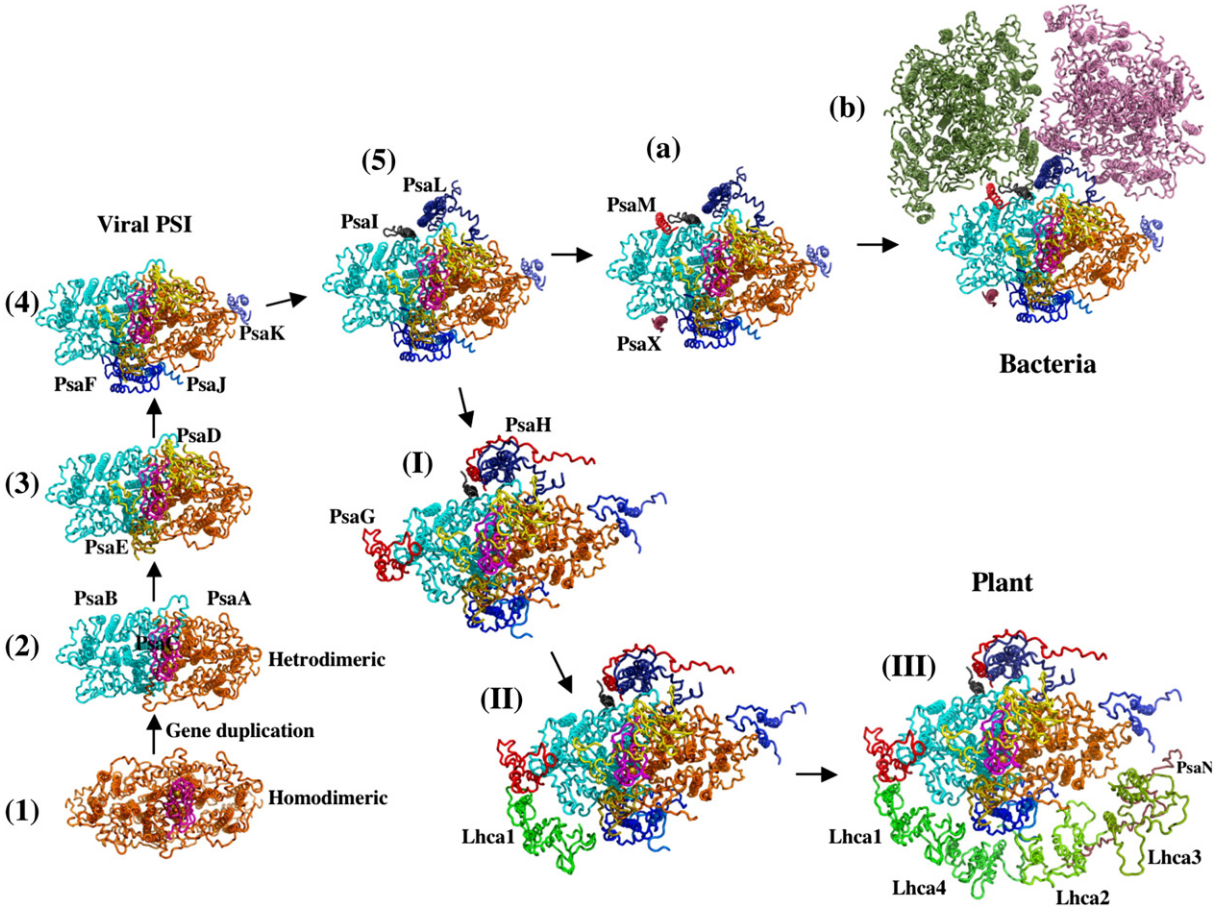

Fig. 4. Proposed events in the evolution of PSI. (1) A homodimeric PSI composed of two PsaA-like subunits and PsaC with two Fe–S clusters as electron acceptor. (2) Gene duplication resulted in two none-identical PsaA and PsaB subunits. (3) PsaD and PsaE are added to improve the ferredoxin binding site. (4) PsaF and PsaJ are added to improve the plastocyanin and/or cytochrome *c* binding site. A variation of this PSI where a PsaJF fusion protein substituted the above subunits is present in the operon of marine viruses [38]. The function of PsaK is not apparent. (5) PsaL and PsaI are added. This may represent the branching point between cyanobacterial and plant PSI. (a) PsaX and PsaM are added to establish the cyanobacteria PSI. The N-terminal extension of PsaL and PsaM facilitate the trimer formation (b). (I) The addition of PsaH and PsaG established the eukaryotic (chloroplast) PSI about 1.5 billion years ago. PsaH prevents trimer formation and PsaG provided a template for the assembly of LHCAI that by the addition of Lhca1 (II). (III) The monomeric plant PSI with its four light-harvesting complexes Lhca1–4.

modality, versatility, tolerance to high light intensity, and near-perfect quantum yield of PSI assisted algae and higher plants in surviving near the surface of water and on land.

6. The contribution of oxygenic photosynthesis to global evolution

Our hydrogen-rich universe has practically unlimited reducing power; in theory, this should suppress most universal downhill electron transfer reactions. However, hydrogen is not sufficient to generate and sustain life forms. As a result of enormous supernova eruptions and other violent cosmic events, heavier elements were formed, which subsequently generated conditions that could sustain life. Of the four biomarkers of habitable planets—water, methane, carbon dioxide, and oxygen (O_2) [39]—the latter is remarkable in being a highly oxidizing agent that is necessarily present in planets that were generated in highly reducing environments. Indeed, among the four biomarkers, only oxygen has yet to be observed in the atmosphere of a planet outside our solar system [40]. These four components are far from being sufficient to sustain life as we know it. Earth also has an abundance of elements comprising nearly the entire periodic table; many of these are vital for the catalysis of biological reactions, and many systems would not be built properly without them. Excluding rare cosmic events, earth is governed by chemical reactions and the second law of thermodynamics. According to this universal law, the entropy of an isolated system that is not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium. One of the biological ideas arising with this concept of entropy is that nature tends to form disorder in isolated systems. Thus, put simply, to increase order in an isolated system (cell, organism, village, town, state, or planet), a constant intake of energy must be established and the waste products (garbage) must be removed. Life on earth is sustained by the constant flow of energy provided by photosynthesis; moreover, during at least four critical events in the evolution of advanced life forms, photosynthesis was necessary to remove excess material from isolated systems. This subject will be discussed as "energy in, garbage out."

Life on earth was initiated and sustained for about 2 billion years under unaerobic conditions in which free oxygen was highly limited [3,39–42]. Under these conditions, energy is plentiful, provided that electron acceptors are available. However, under unaerobic conditions, in which almost every chemical is reduced, electron acceptors are scarce. As the first life appeared on earth, photosynthesis would have been crucial but limited to the formation of energy-rich chemical bonds (such those present in ATP) and the electrons would have flowed in cycles in a process called cyclic phosphorylation (Fig. 1 and ref [2]). Respiration, in which electrons flow downhill, existed, but was limited to the available electron acceptors. When oxygenic photosynthesis came along, it would have turned everything upside down. Water, which is present at exceedingly high amounts on earth but holds its electrons very tightly, became the electron donor for this process. We propose that it was not the plentiful electron donor (which was abundant under unaerobic conditions) that gave the edge to oxygenic photosynthesis, but its ability to throw the garbage out.

About 3.5 billion years ago, during the onset of oxygenic photosynthesis, the only electron acceptor that was relatively abundant was CO_2, and pathways for CO_2 fixation into organic matter were already available at that time. Studies with carbon isotopes suggest that the enzyme ribulose-1,5-bisphosphate carboxylase has controlled the global distribution of carbon in the atmosphere–ocean system for at least 3.5 billion years, selectively mobilizing carbon into the biosphere from an abundant atmospheric reservoir [43–47]. However, the amount of organic matter produced by oxygenic photosynthesis is far too low to explain the amount of oxygen present in the earth's atmosphere. Thus, there is no escape from the idea that an electron acceptor that is no longer present in significant amounts on the earth's surface and atmosphere was available for as long as anaerobic conditions prevailed. The only electron-acceptor candidate that would appear to fit this bill is protons generated by the production of oxygen from water. Indeed, several organisms that perform oxygenic photosynthesis contain the enzyme hydrogenase, which, under strict unaerobic conditions, can convert protons to hydrogen [48–50]. The hydrogen produced by this process diffuses to the upper atmosphere, where its kinetic energy is sufficient for it to gain the velocity necessary for it to escape into the solar system. This process can be thought of as a thermodynamic "garbage out," as mentioned above (Fig. 5).

The hydrogenase activity that produced hydrogen from protons ($2\,H^+ \Rightarrow H_2$) provided an unlimited electron acceptor (H+), the same one produced by oxygenic photosynthesis during the oxidation of water to oxygen ($2H_2O \Rightarrow O_2 + 4\,H^+$). This situation would have allowed cyanobacteria-like organisms to proliferate and produce ever-increasing amounts of oxygen. However, oxygen began to accumulate in significant amounts in the atmosphere only after about 2 billion years had passed since the onset of oxygenic photosynthesis [3,40,44]. Apparently, the oxygen produced during those 2 billion years was reduced back to water by reducing components in the earth's crust, and accumulated in the atmosphere only after this gigantic titration was completed [46,47,51]. Iron oxidation was the main player in this process, which left a large geological mark in the form of banded iron—one of the main iron sources today for steel production. The iron concentrated underground can also be considered as thermodynamic "garbage out." The iron sediments resulting from oxidized iron are

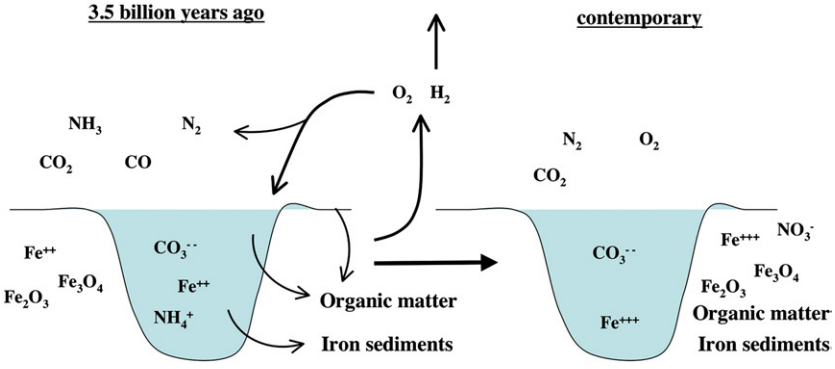

Fig. 5. Global major events resulted from oxygenic photosynthesis. Those events were major contributors for eliminating unused materials (garbage) from the global equilibrating system that shaped contemporary life. 1) Hydrogen produced by oxygenic photosynthesis during the 2 billion years of anaerobiosis escape the atmosphere. 2) Oxygen started to significantly accumulate in the atmosphere in the last 1.5 billion years and reached its peak in the last 200 million years. 3) During the first 2 billion years iron was oxidized by the oxygen produced by oxygenic photosynthesis and the equivalent oxygen reduced back to water. 4) During all the period excess organic material was buried and converted to oil, coal and other sediments that were taken out from the earth surface.

exceedingly less soluble than reduced iron. The decreased amounts of iron and some other metal ions in the oceans drastically changed the metabolism of most organisms; thus, today, instead of concentrating on protecting themselves from the toxic effect of high iron loads, they compete for iron [52]. Essentially, the total mass of organisms in the ocean today (up to and including whales) is limited by the amount of available iron [53,54].

The ancient proliferation of life forms, fueled directly or indirectly by oxygenic photosynthesis, generated excess organic matter. This thermodynamic garbage had to be removed from the equilibrating system. We suggest that the underground petroleum products formed from excess marine organic matter and the coal formed from excess terrestrial organic matter serve as sequestered thermodynamic garbage. As energy consumers, we are lucky that the energy-rich waste products resulting from oxygenic photosynthesis were stored in such a useful form! Similarly, garbage resulting from future large-scale energy production efforts by humans should be treated according to the second law of thermodynamics, with special attention paid to the need for a global garbage disposal. If we are bound to experience the current rate of population growth we will have to send the resulting thermodynamic garbage outside our planet or preferentially outside the solar system.

Acknowledgements

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